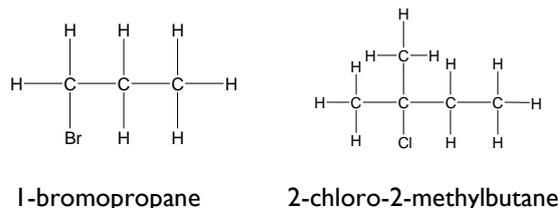


4.2.2 Haloalkanes

Naming Haloalkanes

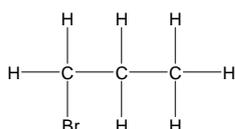
Based on original alkane, with a *prefix* indicating halogen atom:
Fluoro for F; **Chloro** for Cl; **Bromo** for Br; **Iodo** for I.

Substituents are listed **alphabetically**



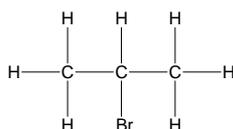
Classifying haloalkanes

Haloalkanes can be classified as primary, secondary or tertiary depending on the number of carbon atoms attached to the C-X functional group.



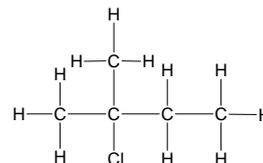
PRIMARY Haloalkane

One carbon attached to the carbon atom adjoining the halogen



SECONDARY Haloalkane

Two carbons attached to the carbon atom adjoining the halogen



TERTIARY Haloalkane

Three carbons attached to the carbon atom adjoining the halogen

Nucleophilic substitution reactions

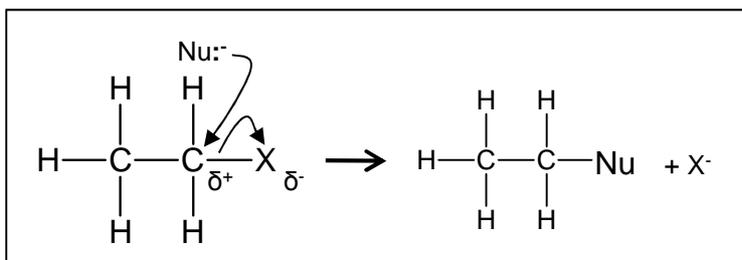
Substitution: swapping a halogen atom for another atom or groups of atoms

Nucleophile: electron pair donor e.g. :OH^- , :NH_3 , CN^-

The Mechanism: We draw (or **outline**) mechanisms to show in detail how a reaction proceeds

:Nu represents any nucleophile – they always have a **lone pair** and act as **electron pair donors**

The nucleophiles attack the positive carbon atom



The carbon has a small positive charge because of the electronegativity difference between the carbon and the halogen



We use curly arrows in mechanisms (with two line heads) to show the movement of two electrons

A curly arrow will always **start** from a **lone pair** of electrons or the **centre of a bond**

The rate of these substitution reactions depends on the strength of the C-X bond

The weaker the bond, the easier it is to break and the faster the reaction.

The iodoalkanes are the fastest to substitute and the fluoroalkanes are the slowest. The strength of the C-F bond is such that fluoroalkanes are very unreactive

	Bond enthalpy / kJmol^{-1}
C-I	238
C-Br	276
C-Cl	338
C-F	484

Nucleophilic substitution with aqueous hydroxide ions

Change in functional group:

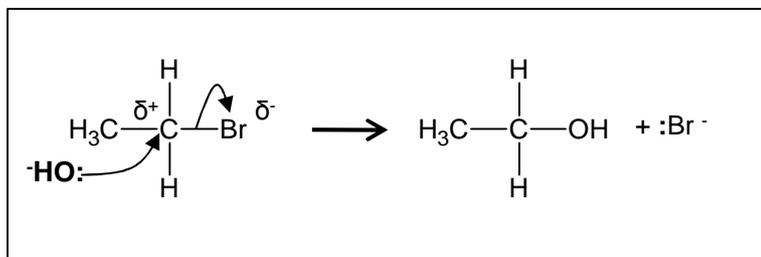
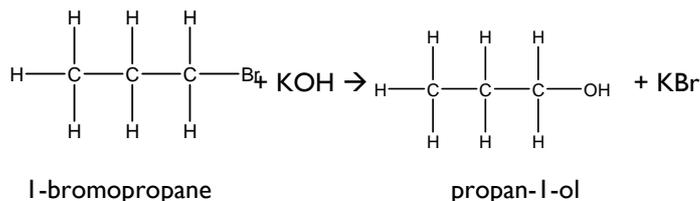
halogenoalkane → alcohol

Reagent: potassium (or sodium) hydroxide

Conditions: In aqueous solution; Heat under reflux

Mechanism: Nucleophilic Substitution

Type of reagent: Nucleophile, OH⁻



The **aqueous** conditions needed is an important point. If the solvent is changed to **ethanol** an elimination reaction occurs

Comparing the rate of hydrolysis reactions

Hydrolysis is defined as the splitting of a molecule (in this case a haloalkane) by a reaction with water



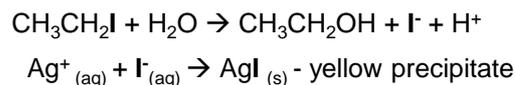
Aqueous silver nitrate is added to a haloalkane and the halide leaving group combines with a silver ion to form a **SILVER HALIDE PRECIPITATE**.

The precipitate only forms when the halide ion has left the haloalkane and so the rate of formation of the precipitate can be used to compare the reactivity of the different haloalkanes.

The **quicker** the **precipitate** is formed, the **faster** the **substitution** reaction and the **more reactive** the haloalkane

The rate of these substitution reactions depends on the strength of the C-X bond . The weaker the bond, the easier it is to break and the faster the reaction.

Water is a **poor nucleophile** but it can react **slowly** with halogenoalkanes in a substitution reaction. Use reflux OR heat for more than 20 minutes



The iodoalkane forms a precipitate with the silver nitrate first as the C-I bond is weakest and so it hydrolyses the quickest

AgI_(s) - yellow precipitate
 AgBr_(s) - cream precipitate
 AgCl_(s) - white precipitate

↑ forms faster

Chlorofluorocarbons (CFC's)

CFC's were developed for use as aerosols, refrigerants, and in air-conditioning due their low reactivity, volatility and non-toxicity.

Many of these uses have now been stopped due to the toxicity of halogenoalkanes and also their detrimental effect on the ozone layer in the atmosphere

Legislation to ban the use of CFCs was supported by chemists and chemists have now developed alternative chlorine-free compounds

HFCs (Hydro fluoro carbons) e.g.. CH₂FCF₃ are now used for refrigerators and air-conditioners. These are safer as they do not contain the C-Cl bond

CO₂ is now used as a blowing agent for producing expanded polymers instead of CFC's

The Ozone Layer

The naturally occurring ozone (O₃) layer in the upper atmosphere is beneficial as it filters out much of the sun's harmful UV radiation

Ozone in the lower atmosphere is a pollutant and contributes towards the formation of smog

Ozone is continuously being formed and broken down in the stratosphere by the action of ultraviolet radiation

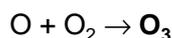


Ozone formation

UV light causes an O₂ molecule to split into free radicals



When the free radical hits another O₂ molecule ozone forms



Ozone depletion

This is the reverse of the formation reaction..

The energy is supplied by ultraviolet light



There is a continuous cycle of formation and depletion of ozone

rate of ozone formation = rate of ozone removal

So there is a constant amount of ozone in the atmosphere

The frequency of ultra-violet light absorbed equals the frequency of biologically damaging ultra-violet radiation. These reactions therefore filter out harmful UV and allow life to survive on earth. UV light can increase risk of skin cancer and increase crop mutation.

Chlorine radicals are formed in the upper atmosphere when energy from ultra-violet radiation causes C-Cl bonds in chlorofluorocarbons (CFCs) to break

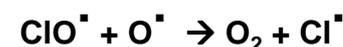
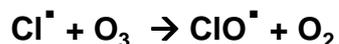


Destruction of Ozone Layer

Radicals from CFCs, and NO_x from thunderstorms or aircraft, may catalyse the breakdown of ozone

The chlorine free radical atoms **catalyse** the decomposition of ozone due to these reactions because they are regenerated. (They provide an alternative route with a lower activation energy)

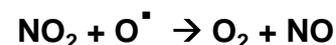
They contributed to the formation of a hole in the ozone layer.



Overall equation



The regenerated Cl radical means that one Cl radical could destroy many thousands of ozone molecules



Overall equation



Legislation to ban the use of CFCs was supported by chemists and that they have now developed alternative chlorine-free compounds

HFCs (Hydro fluoro carbons) e.g.. CH₂FCF₃ are now used for refrigerators and air-conditioners. These are safer as they do not contain the C-Cl bond

CFC's still concern us because CFCs are still entering the atmosphere from disused items and are still used for some purposes and by some countries.

CFCs have a long lifetime in the atmosphere and it takes a long time for CFCs to reach upper atmosphere.